EFFECT OF SOLVENTS ON THE ELECTRONIC ABSORPTION SPECTRUM OF 2-OXY-QUINOXALINE

E. TOMBÁCZ

Institute for General and Physical Chemistry, The University, Szeged

(Received May 15, 1960)

A specific effect of the solvent in dioxan and diethyl-ether was found at the ultraviolet absorption spectra of 2-oxy-quinoxaline. This effect seems to be due to the formation of the complex or to the proton migration between the solvent and the 2-oxy-quinoxaline.

A great deal of theoretical and experimental work has already been devoted to the elucidation of the effect of solvents on the electronic absorption spectra of organic molecules. In earlier papers the band displacement relative to the vapour state was considered as a function of the refractive index [1], in later papers more complex formulae were given taking into account both the refractive index and dielectric constant of the solvent [2]. According to the formula derived by MC RAE and used in a simplified form by R. POPOVICH and B. ROGERS the absorption band displacement

$$\Delta\bar{\nu} = a\frac{n^2-1}{2n^2+1} + b\left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right),$$

where $\Delta\bar{\nu}$ means the displacement of the absorption maximum relative to an arbitrary solvent in wave numbers, n and D denote the refractive index (referring to the D-line of Na) and the dielectric constant of the solvent, respectively, a and b are constants, which for a given class of solvents depend only on the solute. By means of this equation R. POPOVICH and B. ROGERS investigated the effect of solvents on the absorption spectra of 8-quinolinol and its Zn-chelate. Recently I. A, ZHMYREVA, V. V. ZELINSKY and their coworkers carried out similar researches on 4-aminophtalimide [3]. The aim of this paper is to investigate the influence of solvent on 2-oxy-quinoxaline by means of the equation given above.

The ultraviolet absorption spectra of 2-oxy-quinoxaline were obtained with a Beckman DU spectrophotometer in nine different solvents shown in the first column of the table. All the solvents were specially purified for spectroscopical purposes according to the usual methods (see *e. g.* in [4]). The compound to be investigated was carefully purified and according to [5] it was found to be sufficiently pure. Characteristic properties of the sol-

vents used are seen in the second and third column of the table and were taken from the literature [6]. The values of ν_{max} in cm^{-1} for different solvents and for the band of greatest wavelength are included in the fourth column and the error in the determination of the position of the band maximum is estimated to be about $\pm 25\,cm^{-1}$. Considering the highest value of $\bar{\nu}_{max}$ at chloroform as reference solvent, the measured values of $\Delta\bar{\nu}_{max}$ relative to the reference $\bar{\nu}_{max}$ are tabulated in the fifth column. The constants a and b were calculated by substituting two measured $\Delta\bar{\nu}$ values into the equation; the data for two pairs of solvents (ethanol and 2-pentanol, water and propanol) yielded the mean values for the constants: $a = -8410\ cm^{-1}$, $b = 3170\ cm^{-1}$. By means of these empirical constants the band displacements were calculated for all the solvents used are tabulated as $\Delta\bar{\nu}_{calc.}$ values in the sixth column.

Table I

1	2	3	4	5	6
Solvent	n	D	$\bar{\nu}_{max}$	$\Delta\bar{\nu}_{meas}$	$\Delta\bar{\nu}_{calc}$
			in cm^{-1}		
Water	1,332	81,0	28 570	1010	971
Methanol	1,331	35,7	28 820	760	804
Ethanol	1,363	26,8	28 950	630	600
Propanol	1,385	22,2	29 180	400	436
Butanol	1,399	19,2	29 280	300	302
2-pentanol	1,409	14,3	29 440	140	138
Chloroform	1,44	5,14	29 580	0	—791
Diethyl ether	1,354	4,4	29 280	300	—605
Dioxane	1,442	3,0	29 410	170	—1242

A comparison of $\Delta\bar{\nu}_{meas.}$ and $\Delta\bar{\nu}_{calc.}$ shows that these values are in a good agreement at water and alcohols, the difference between measured and calculated band displacements is within the range of the estimated error. A very great discrepancy is to be observed at chloroform, diethyl ether and dioxane. In order to clear up the cause of this discrepancy the whole absorption spectra were investigated. For the sake of a better survey the figure shows only four selected spectra. Comparing all the spectra it is easy to observe that these fall into two groups, the one group exhibits a maximum or shoulder at a wave number 40 000 cm^{-1} (similarly to curves 1 and 2), the second group, however, shows no sign of such a maximum or shoulder (similarly to curves 3 and 4). The band displacements of all the absorption curves belonging to the one group may be calculated by the Mc RAE equation, while those of the second group may not be given by calculation.

This behaviour of the spectra may be explained by an alteration of the character of interaction between solvent and solute molecules when turning from the one group of solvents to the second group. Water and alcohols behave predominantly as a continous polarizing medium and suppress the specific interaction, if it exists at all, therefore the measured and calculated

band displacements coincide. Chloroform, diethyl ether and dioxane have a considerable smaller polarizing effect, consequently these solvents give a possibility for the developing of specific interactions between solvent and solute molecules. The disappearance of the maximum or shoulder at a wave number of 40 000 cm^{-1} at the latter solvents is a sign of this specific interaction, which may consist in a proton donation to the solvent molecule.

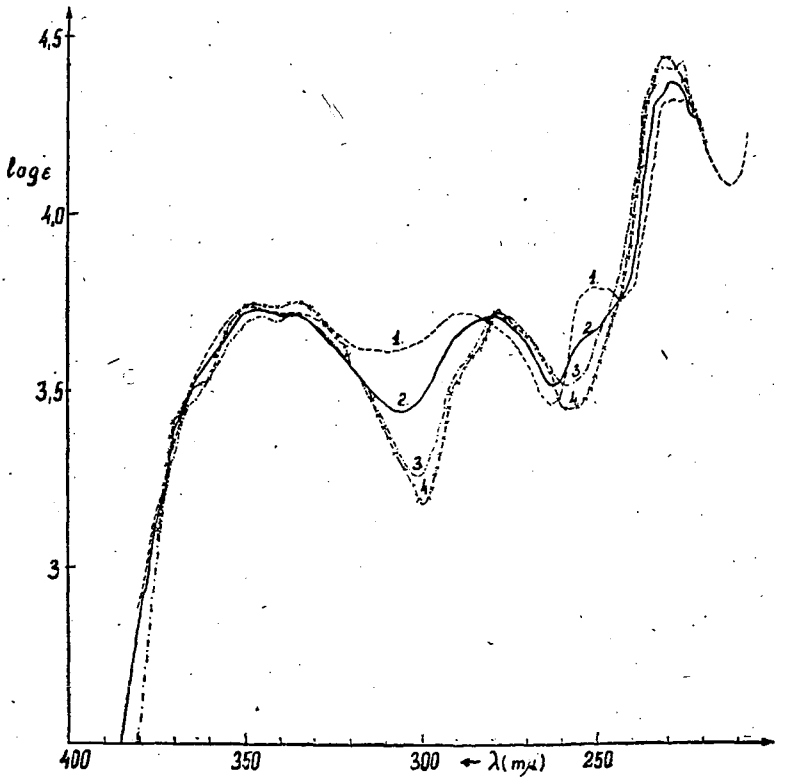

Fig. 1

This supposition seems to be verified by the results of [5]. Though nitrogen has proton-acceptor properties, the N-atom in 2-oxy-quinoxaline is not saturated but capable for proton acception or donation according to its surroundings. Even in water pH-values were to be found at which the maximum or shoulder at a wave number of 40 000 cm^{-1} could not be detected and this change in the spectrum undoubtedly seemed to be in connection with a proton acception or donation. It is not excluded either, that the specific interaction is due to a complex formation between the solute and solvent molecules; the free electron pairs of chloroform, diethyl ether and dioxane may cause a formation of assotiation complexes of 2-oxy-quinoxaline with the solvent molecules.

* * *

Thanks are due to professor Á. KISS, the director of the institute for his kind help and interest.

References

[1] *Bayliss, N. S.:* J. Chem. Phys., **18**, 292 (1950).
[2] *Ooshika, Y.:* J. Phys. Soc. Japan, **9**, 594 (1954);
McRae, E. G.: J. Phys. Chem., **61**, 562 (1657);
Popovych, O., L. B. Rogers: J. Amer. Chem. Soc.. **81**, 4469 (1959).
[3] Жтирева, И. А., В. В. Зегипский, В. П. Коловков, А. С. Коцетировский и И. М. Резникова: Опт. и Спектр. **8**, 412 (1960).
[4] *Weisberger, A., E. S. Proskauer, J. A. Riddick, E. E. Toops:* Organic Solvents. Technique of Organic Chemistry, Vol. VII. (Interscience Publishers, Inc., New York, 1955.)
[5] *Tombácz, E.:* Acta Phys. Chem. Szeged, **3**, 56 (1957).
[6] *Heilbron, I., H. M. Bunbury:* Dictionary of Organic Compound (London, 1946).

ВЛИЯНИЕ РАСТВОРИТЕЛЕЙ НА ЕЛЕКТРОННЫЕ СПЕКТРЫ ПОГЛОЩЕНИЯ 2-ОКСИ-КИНОКСАЛИНОВ

Е. Томбац

У ультрафиолетового спектра поглощения 2-окси-хиноксалина найден в диоксане и диэтилэфире специфический эффект растворителя. Повидимому этот эффект заключается в образовании комплексов или в миграции протонов между 2-окси-хиноксалином и растворителем.